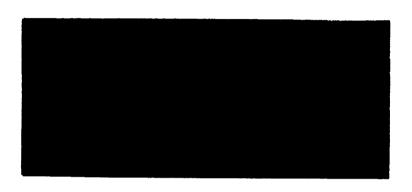
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Alkaline Battery Division

GULTON INDUSTRIES, INC.

Metuchen, N. J.

t: Design, Development and Manufacture

OF STORAGE BATTERIES FOR FUTURE

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EIGHTH QUARTERLY PROGRESS REPORT

4 August 1962 to 4 November 1962

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I. ABSTRACT

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The prototype VO-50 HS cells are being completed and 10 have been delivered. These cells have an energy capability of 18.5 watt hours per pound.

Continued study of the thin plate cells has demonstrated their capability to perform well at high rates and also to cycle continuously in a 35% depth routine, but as pointed out in the Seventh Quarterly Report no advantage is seen in the watt hour per pound capability of these cells as compared to the thicker plate standard line of cells.

VO-6 HS cells have so far been successfully cycled 1500 cycles at 70% depth of discharge at 77°F and 1440 cycles at 50% depth of discharge, at 77°F. Both cycle tests are still in progress.

Charge efficiency studies at 77° to 120°F show that early in the charge the inefficiency of the negative electrode causes evolution of hydrogen gas. This is particularly true at high charge rates and low temperatures. Studies were performed on the self-discharge (oxygen evolution) rate of positive electrodes at several temperatures and after different charge rates. Also studied was the pressure decay in cells into which oxygen had been introduced after charge at several different rates.

II. 50 A. H. HERMETICALLY SEALED CELLS

The formation of the electrodes for the 50 AH hermetically sealed nickel-cadmium cell has been completed. The cell packs were unwrapped and the plates cleaned and dried. In order to minimize fluctuation because of individual cell characteristics, both the positive and negative electrodes were randomized before the electrode stacks were fabricated.

Five cells were selected for testing from the group that was already sealed and checked for leakage. Electrolyte was added to each before the valves and pressure gauges were attached to the pinch tubes. Two of the cells, Nos. 103 and 104, were charged and overcharged at a C/10 rate for 41 hours. After a four (4) hour stand time, they were discharged at the C/2, 25 amperes, rate. The average capacity to 1.0 volt was 57.7 A.H.

The two cells were then charged at a C/10 rate and maintained for 40.5 hours to insure that a steady state was established. The pressures for Nos. 103 and 104 were 47.5 psig and 51.5 psig, respectively. The cell voltage for both was 1.40 volts. To determine the effect of cycling, both were placed on a 100 minute cycle. They were discharged at 20.0 amperes for 36 minutes and charged at 13.5 amperes for 64 minutes. After 12 cycles they were overcharged at the C/10 rate for 23.3 hours. The pressures for cell No. 103 and cell No. 104 were 35.5 psig and 41.0 psig, respectively, while the cell voltage for both was 1.38 volts.

The two cells were discharged at the C/2 rate as shown in Figure 1. The average capacity to 1.0 volt was 58.5 empere-hours. The end of discharge pressure for cell No. 103 was -10 inches gauge

and the end of discharge pressure for cell No. 4 was -20 inches gauge.

In order to show the overcharge characteristics, the two cells were placed in an oil bath which was maintained at 25 ± 0.5°C. The cells were given a C/10 charge which was maintained for 163.3 hours to insure steady state conditions. The average cell voltage was 1.42 volts and the average cell pressure was 65.3 paig. The current was them raised to C/5 and maintained until a steady state was obtained. The average cell voltage was 1.43 volts while the average cell pressure was 127 paig. This information is shown in Figures 2 and 3.

at a C/10 rate for 41.3 hours. They were then cycled under the conditions stated above, i.e. discharging at 20.0 amperes for 36 minutes and charging at 13.5 amperes for 64 minutes. At the end of cycle 12 charge the cell voltages and pressures were recorded. These are given in Table 1. In order to determine the effect of cycling on the cell capacity, first the cells were overcharged at the C/10 rate for 24.8 hours. The cell voltages and pressures are recorded in Table 1. Then a C/2 rate discharge was conducted and the average capacity to 1.0 volts was 58.0 ampere-hours. The end of discharge pressures (at 1.0 volt) are given in Table 1.

The three cells were charged and overcharged at the C/10 rate for 72 hours. A C rate discharge was conducted. The capacity to 1.0 volt,51.5 ampere-hours, 1s shown in Figure 1. The cell voltages and pressures immediately prior to C rate discharge and at the end of discharge (at 1.0 volt) are given in Table 1.

The data presented here shows a consistency in cell performances. The capacity at the C/2 rate discharge for cell No. 103 and No. 104, and cell No. 105 through No. 107 show a difference of 0.5 ampere-hours (0.86%).

TABLE 1 CHARACTERISTICS OF VO-50 HS CELLS

CELL #105 CELL #106 CELL #107

	Cell Voltage V.	Pressure p.s.i.g.	Cell Voltage V.	Pressure p.s.i.g.	Cell Voltage V.	Pressure p.s.i.g.
				·		
End of Charge, Cycle 12	1.45	14.5	1.44	13.5	1.45	12.5
Steady State Values at C/10 Overcharge	1.38	59.0	1.3 8	54.0	1.39	44.5
After <u>C/2</u> rate Discharge (at 1.0 volt)	1.00	-10"	1.00	-5"	1.00	-9"
Steady State Values at C/10 Overcharge	1.38	53.5	1.38	52.0	1.38	44.5
After C Rate Discharge (at 1.0 volt)	1.00	5.0	1.00	6.0	1.00	4.0

The C rate discharge, shown in Figure 1, illustrates the range of individual readings. The small variations indicate good uniformity in cell voltages. The range in cell pressures is shown in Table 1.

The overcharge characteristics show a slope steeper than for a VO-20 HS nickel-cadmium cell.

Test data for the three cells delivered 11/20/62 are shown in Table 2. Test data for the 7 cells shipped 12/12/62 are shown in Table 3.

TABLE 2 TEST HIS ONE OF GULTON 50 E. S.

HERMALICALLY SEALED CELLS FOR

		1				
OVERCHARGE FOR 24 HOURS AT 5.0 AMPS.		ONCLE FUR 10 CYCLES	WEACHTY CLEAR O'SCHANNED AL 25.0 ANPS. TO 1.0 VOLT	SHORTED FOR 16 HOURS; CHARGE) FOR 5 MINUTES AT 5 AM DRESSON OFEN CIRCUIT STAND FOR 24 HOURS		
VOLT.	FRESSURE		A. H.	0. C. V.		
1.38	59.0	36	56.7	1.20		
1.38	54.0			1.20		
1.39	44.5	AT 20.0 AMPERES	58.3	1.20		
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	24 HOUT AT 5.0 VOLT. 1.38	24 HOURS AT _5.0 AMPS. VOLT. FRESSURE 1.38 59.0 1.38 54.0	24 HOURS 10 CYCYES VOLT. FRESSURE 1.38 59.0 36 1.38 54.0 DISCHARGE AT 20.0 AMPTRES 64 *** : CYCYES 64 *** : CYCYES	24 HOURS 10 CYCLES 25.07.NPS. TO CYCLES 1.0 /CLT VOLT. FRESSURE A. H. 1.38 59.0 36 56.7 1.38 54.0 DISCHARGE AT 20.0 AMPRIL. 64 28 11 UFFE CUARGN AT 13.5 AMPRILES		

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TABLE 3

TEST HISTORY OF GUITON WO-50 H. S.

HERMETICALLY STAIRD CELLS FOR

____NASA____

<i></i>						
CELL NUMBER	24 / 100	CVERCHARGE FOR 24 JOURS AT 5.0 AMPS.		CATACITY CHECK DISCHARGED AT 25.0AMES. CO	GHURTED FOR 16 HOURS; CHURGED FOR 5 MINUTES AT 5.0 AMPERES ON OPEN CIRCUIT STAND FOR 24 FOURS	
	VOLT.	PRESSURE		A. H.	c. c. v.	
100	1.39	35.5	36	59.20	1.19	
101	1.39	41.0	MANUTE ALL	53.90	•	
107	1.38	51.0	DISCHARGE AT 20.0	59.17	1.17	
108	1.38	15.0	AM ERES	64.18	1,18	
109	1.38	30.0		59.17	1.16	
111	1.38	35.0	,	60,01	1,17	
115	1.38	46.0	64 XX N.1N TO	58.76	1.19	
			CHARGE			
			AT 13.5 AMPERES			
			_ ,, .,			
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III. THIN PLATE CELLS

The VO5X thin plate cells have already been subjected to a series of tests. In the last quarterly report, the overcharge characteristics were given. In addition the capacities at various C rate discharges were reported. After the final C/2 rate discharge, indicated in the report, the cells were charged and overcharged at 0.5A for a period of ten (10) days. The average cell voltage at the end of the overcharge was 1.40 volts and the average cell pressure was 14.0 p.s.i.g.

The thin plate cells were then put on 90 minute cycling. They were discharged to a 35% depth at 3.0 amperes for 35 minutes, 1.75 A.H., and charged (115%) at 2.19 amperes for 55 minutes, 2.01 A.H. To date 1012 cycles have been completed. Table 4 shows the average cell voltages at the beginning and the end of discharge as well as at the beginning and the end of charge for several cycles. In addition, the end of charge pressures are recorded at these cycles. It was observed that the end of discharge voltage has slowly decreased with cycling.

TABLE 4

CELL CHARACTERISTICS FOR THE VO5X AT VARIOUS CYCLES

	Disc	Discharge		rge	End of Charge	
Cycle No.	₹0	E35	E _O	E55	Pressure, p.s.i.g.	
17	1.35	1.21	1.27	1.46	2.0	
531	1.36	1.17	1.24	1.49	15.4	
1012	1.35	1.14	1.23	1.48	8.2	

IV. ELECTRICAL PERFORMANCE OF VO-6 HS CELLS

Cycling

The five experimental VO-6 HS type cells which had been cycled 800 times were placed back on cycle after a capacity check. The 90 minute cycle consists of a 35 minute discharge at 7.2 amps or a 70% depth of capacity followed by a 55 minute charge at 5.5 amps or a 20% overcharge.

At about the 850th cycle one of the cells was observed to exhibit a decreasing end of discharge voltage and a rising end of charge voltage. This continued with increasing magnitude. At the 926th cycle this cell indicated a short and it was removed and disassembled for failure analysis. The separator was very dry and there was a short burned through the separator at one of the corners. At the 960th cycle another cell similarly failed.

The remaining three cells have completed over 1500 cycles and the end of charge voltages average 1.57 and the end of discharge charge voltages average 1.00. A change in charge current of .05 amps was detected and corrected so that the end of discharge voltages should return to the 1.04 volts which is the usual level for this cycle.

Another set of VO-6 HS cells has been on automatic cycle since August 20, 1962, at a 50% depth of discharge and a 90 minute cycle. This cycle consists of a 35 minute discharge at 5.15 amps and a 55 minute charge at 3.86 amps or an 18% overcharge. A typical plot of cycle #1440 is shown in Figure 4.

A plot of the average end of charge voltages and end of discharge voltages vs. cycle number is shown in Figure 5. The fluctuation in end of discharge voltage at the beginning was due to instability in the cycling current. Since at this depth of cycle, only 18% overcharge is necessary to maintain an end of discharge voltage above 1.00 volts, instead of 20% overcharge, it is also more critical to maintain the current constant. A drop of 0.06 amps on charge means a change from 18% overcharge to 16% overcharge which is not enough. If the overcharge is increased above 18% to allow a greater safety factor, the end of charge voltages are higher. It is desirous to maintain the lowest practical charge current to keep the pressure low without losing capacity.

V. CHARGE EFFICIENCY STUDIES

A. INTRODUCTION

The charge efficiency of nickel-cadmium cells has always been less at low temperatures (less than $60^{\circ}F$) and elevated temperatures (more than $80^{\circ}F$) than at room ambient temperatures (70° to $80^{\circ}F$). Since recent work on self-discharge processes of the positive electrodes show these to be strongly temperature dependent , one possible explanation of the high temperature efficiency phenomenon is simply that the positives can not be adequately charged.

The charge efficiency at lower temperatures, on the other hand, appears to be dependent upon the negative electrode. When cells are charged at low temperatures, hydrogen is frequently found. This implies a passivation of the negative electrode and accounts for our previous observation.

When current is passed through a cell an electrode process must occur at each electrode. This process, which is a charge transfer process, accounts for the simultaneous electron flow in the external circuit and ion flow between the electrodes. If we let this current be denoted as i, then each process that occurs at an electrode occurs at a rate which may be written as ip, where the p denotes an electro-chemical process. For instance, at the positive electrode there is an oxidation of nickelous hydroxide during charge,

1) Ni^{II} \longrightarrow Ni^{III} + C , i_{Ni} , and there may be a simultaneous oxidation of hydroxyl ions to yield oxygen,

2)
$$40H \rightarrow 0_2 +2H_20 + 4e^-$$
 , i_0 .

Since $i + i_0$, the rate of oxygen formation is a charge inefficiency.

While the reactions given by equations 1 and 2 are an adequate heuristic representation they do not convey all that is known about the charge processes. For instance, evidence has been obtained for the existence of several higher oxides of Ni. 1,2 The overcharge reaction may not simply be the oxidation of hydroxyl ions, but it may equally well be that the rate of self-discharge of the higher oxides of Ni is very great and the decomposition rates are determined by the charge current. Consider for a moment the fact that a nickel oxide electrode charged at atmospheric pressure does not exhibit a voltage step at the end of charge. This absence of a voltage step is not inconsistent with the explanation of a rapid self-discharge in the domain of overcharge. Since the rapid self-discharge processes are apparently temperature dependent, this theory would help account for a decrease in charge efficiency of positive electrodes at elevated temperatures.

In a similar way, the negative electrode may decrease its efficiency at lower temperatures for another reason. Heuristically we may consider the charge reactions as follows:

3)
$$Cd(OH)_2+2 \longrightarrow Cd + 2 OH^-$$
, ¹Cd

4)
$$2H_2O + 2 \longrightarrow H_2 + 2 OH$$
, i_{H_2}

The charge efficiency of the negative electrode (at constant i) is therefore defined by the expression i_{Cd}dt/idt. The Cd/Cd(OH)₂ electrode exhibits a voltage step during charge at atmospheric pressure.³ At this point elemental hydrogen is produced. This step in voltage with its corresponding change in process is termed passivation of the electrode. The passivation of the Cd/Cd(OH)₂ arrives earlier when the charge rate is increased, and when the temperature is decreased.

Studies of the charge efficiencies are of importance in evaluating the theories, which in turn will enable one to make improvements in charge efficiencies. In the work about to be described, the point at which pressures in sealed cells start to change and the identification of the gases in the atmosphere above the electrodes are used to determine the onset of the competitive reactions io and iH which give rise to the observed inefficiencies.

B. EXPERIMENTAL PROCEDURES

Eight laboratory type 6 AH nickel-cadmium sealed cells equipped with Marsh pressures gauges were prepared (See Figure 6). The cells were then given four stabilization cycles as follows:

Charge of 0.6 A for 20 hours (12 AH input)
Discharge at 3 A to 1.0 volt

The cells were then placed in constant temperature baths at 77°, 90° , 100° and 120° F. Following this, the cells were grouped and charged at 0.6A (C/10), 1.2A (C/5), 3A (C/2) and 6A (C) at each temperature given above. The charges were taken either to 150 psig or steady state pressure. During the charge, pressure versus time data were taken. In addition, the gases in each cell were collected and tested for hydrogen or oxygen. The charge was then stopped; the cells were evacuated (while remaining in their respective temperature baths) and the pressure rise with time was measured.

Following these determinations, the cell pressure was raised to 50 psig with oxygen. Thereafter the changes in cell pressure with time were measured.

At the completion of a test series (charge, stand for self-discharge and pressure decay after pressurization to 50 psig O_2), each cell was discharged at 3A to 1.0 volt for capacity.

C. EXPERIMENTAL RESULTS

In Figures 7-10 we have plotted pressure change versus charge input for the cells at the various charge currents and temperatures. These data indicate, that in general, as the charge current is increased, the cells tend to gas at progressively lower inputs. Furthermore, at low charge currents (0.6 and 1.2 amperes), the gas in the cell was oxygen,

while at high charge currents (3.0 and 6.0 amperes), hydrogen was present in large quantities. Under the experimental conditions, steady-state pressures were reached only with the lower currents, namely C/10 and C/5. However, at the higher currents, hydrogen was formed early in the charge, indicating passivation of the negatives, and the pressure increased steadily to the gauge limit of 150 psi.

The ampere-hour inputs as a function of charge current are shown in Figure 11. At low charge rates there is a slight increase in charge input required to produce gas as the temperature is raised.

The self-discharge curves of the various cells after charge interruption under the conditions of this experiment are shown in Figures 12-15 in terms of oxygen pressure. An examination of these curves shows that the pressure in each case rises relatively rapidly to a given level, plateaus at this level and then decays. The initial rates of pressure rise tend to increase with increasing temperature and charge current, while the dwell time at the plateau decreases with increasing temperature.

Pressure decay curves for the experimental cells at the four temperatures and four corresponding charge rates are shown in Figures 16-19. There is a tendency for faster decay at elevated temperatures, and the apparent slower recombination rate as the charge rate increases is probably due to the fact that after a higher rate charge, oxygen is being released at a higher rate and offsets some of the pressure decay characteristic.

The cell capacities obtained after discharge at 3A to 1.0 volt are listed in Table 5.

TABLE 5

CELL CAPACITIES AFTER DISCHARGE AT
3A TO 1.0 VOLT AT INDICATED TEMPERATURES

Charge Current	Temperature OF						
Amperes	<u>77</u>	90	100	120			
0.6	6.6	6.9	6.4	6.1			
1.2	6.6	7.0	6.7	6.4			
3.0	7.4	7.3	6.4	6.5			
6.0	7.5	7.3	6.3	6.3			

D. DISCUSSION

Charge efficiencies of less than unity may be due to (1) the oxidation of water at the positive to form oxygen, or an equivalent electrochemical reaction (2) the reduction of water at the negative to yield hydrogen, as given above by equations

(2)
$$40H^{\circ} \longrightarrow 2H_2O + O_2 + 4C^{-}$$
 and

Nuring the charging of the cells in the experimental scheme, both reactions were in evidence as shown by the tests for hydrogen and oxygen (see Figures 7-11). At high charge rates, hydrogen was always formed at a point during the charge when the input was less than the rated cell capacity. Therefore, it is seen that low efficiency, even at elevated temperatures is primarily due to a charge efficiency of less than unity at the negative electrode. The positive electrode, at these relatively high charge rates must then be significantly more efficient than the negative. If the positive was significantly less efficient than the negative, the evolved oxygen would travel to the negative and depolarize it by reaction with hydrogen to form water.

The difference in charge efficiencies between the positive and negative electrodes indicated by Figures 7-11 is again suggested upon examination of Figures 12-15. There is an increase in self-discharge* (oxygen evolution) rate with charge rate and temperature tor the positives. This causes the capacities of the positives to reach a maximum. Therefore, the higher charge rates do not result in a more efficient charge.

^{*}The self-discharge processes involved are the fast processes which have half-times of 8 minutes and 150 minutes, approximately. There is no experimental evidence for a faster self-discharge of ENIOOH, and, in our opinion, no such evidence will ever be found.

It is well known that the decay characteristics of each cell differ, possibly because of surface factors. Furthermore, these surface factors appear to change with each charge. In spite of the inherent scatter in the data, no correlation is found between charge rate and pressure decay (Figures 16-19). This is not an unexpected result.

Since the cells were charged at the low rates to steady state oxygen pressure and at the high rates to 150 psig hydrogen pressure, the charge input in each case was different. Consequently, cell capacities after 3A discharge to 1.0 volt, as given in Table 1, afforded no information with regard to cell efficiency, although it may be seen that at 77°F, the capacities increase at the high charge rates. However, the beneficial effects of the higher charge rates are lost as the temperature is increased.

VI. PROGRAM FOR NEXT PERIOD

The balance of the VO-50 HS cells will be completed and delivered.

The cycling of VO-6 HS cells to 50 and 70% depths of discharge will continue.

Charge efficiency studies will continue and will include:

- Cold temperature charge tests will be carried out at temperatures of -15°, 0°, 25° and 50°F.
- 2. The tests will be performed under the following charge conditions:
 - a. Constant current
 - b. Constant potential

These methods require some explanation. In the constant current method, the current will be set low enough to prevent excessive pressure buildup in the cells. Therefore, the charge rates will be set at C/10, C/20 and C/40. When employing a constant potential charge, the current decreases with time asymptotically to some final value which may permit overcharge accompanied by low cell pressure. To obtain an indication of the maximum safe charge potential, constant potential charges will be carried out at 1.45, 1.50, 1.55 and 1.60 volts. This latter information will be of significant use in applying these sealed cells to satellite applications.

VII. REFERENCES

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- 2. J. L. Weinenger and M. W. Breitner, Paper presented at the sessions at the Electrochemical Society, Boston, 1962.
- 3. Casey and Lake, Journal of the Electrochemical Society, Vol. 105 (1958)

VIII. PERSONNEL

The following staff personnel worked on this project during the past quarter:

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CHEAICAL ENGINEER

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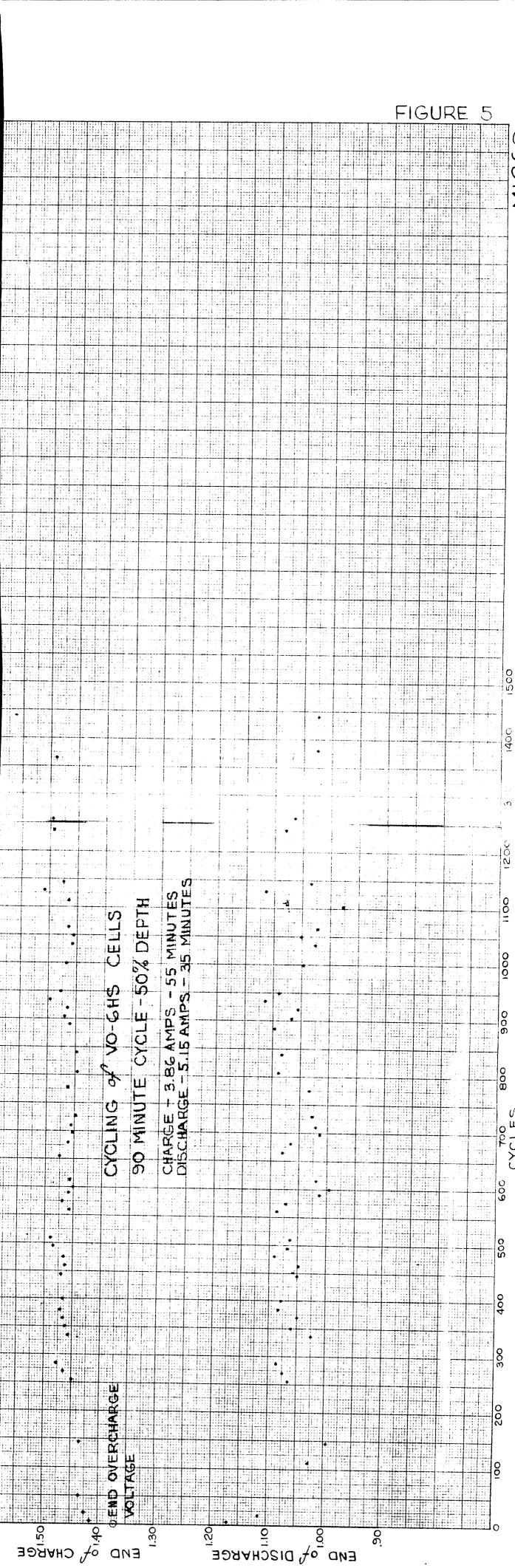
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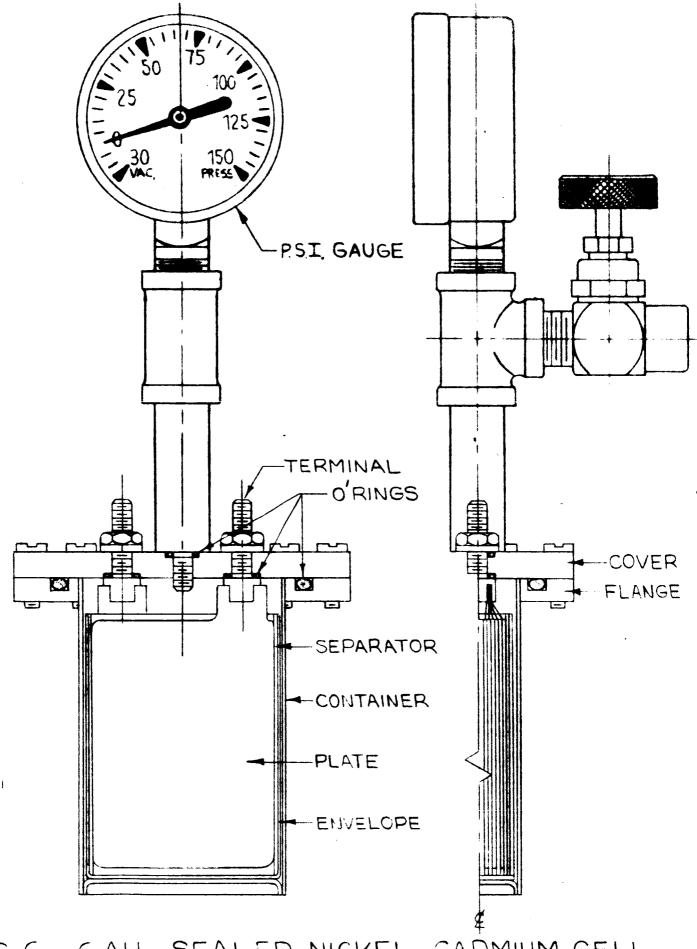
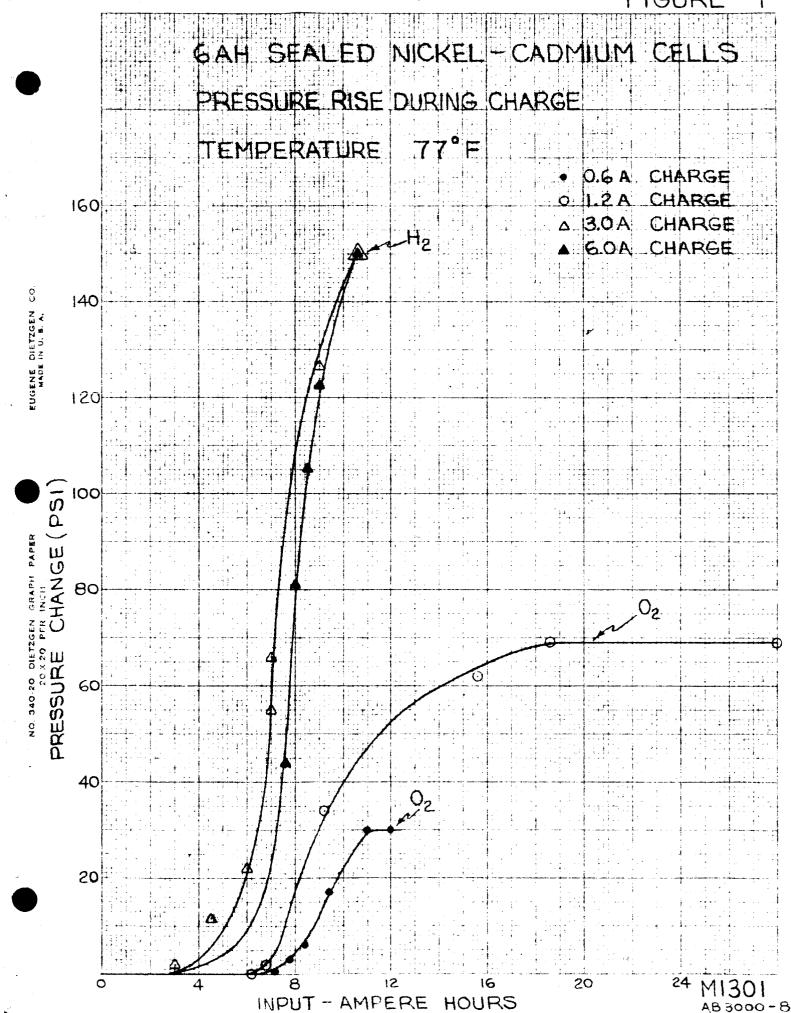
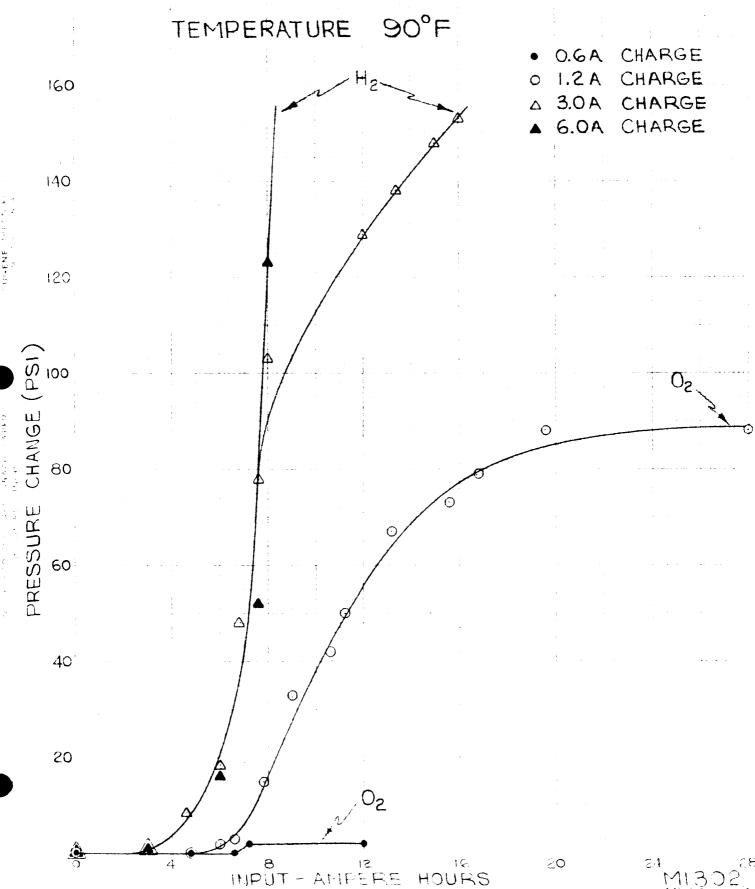


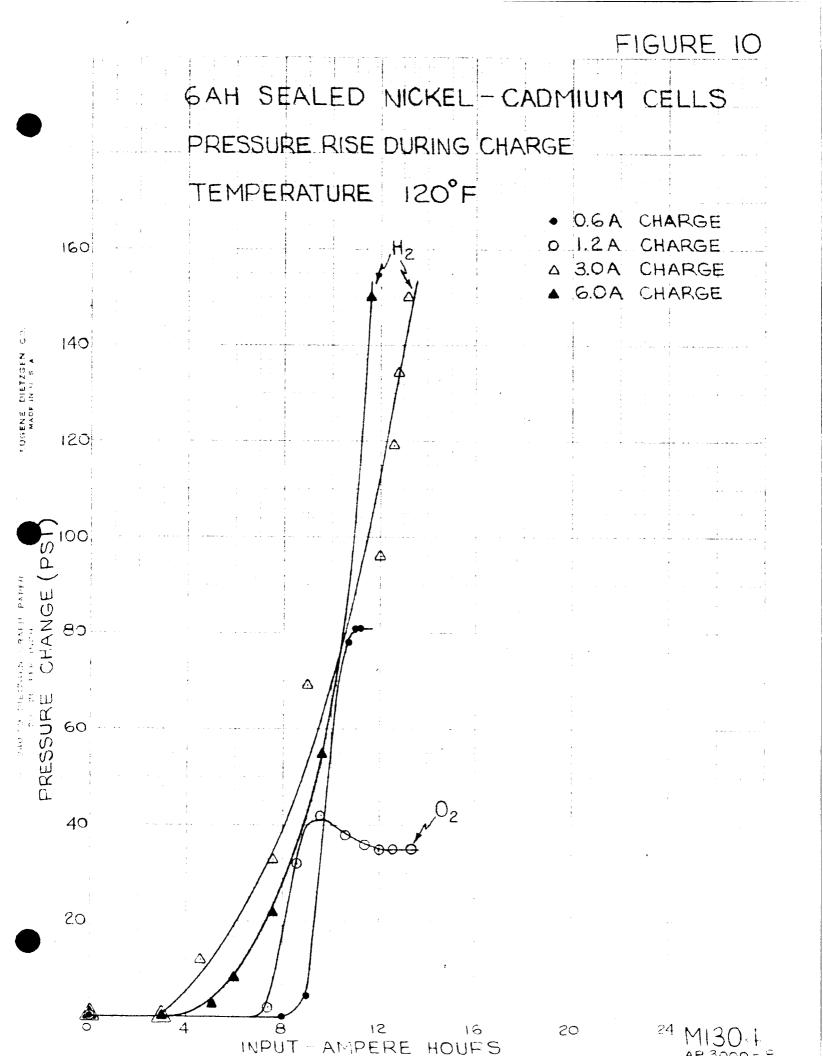
FIG. 6 - 6 AH SEALED NICKEL-CADMIUM CELL

M1239



6AH SEALED NICKEL - CADMIUM CELLS
PRESSURE RISE DURING CHARGE





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M1307 AB 3000-8

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MI308 AB3000-8

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